A specific formation of an iridium(III) hydrido complex bearing 8-(diphenylphosphino)quinoline

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Abstract

A reaction of [Cp*IrCl(Ph_2Pqn)]PF_6 {Cp* = η^5-pentamethylcyclopentadienyl; Ph_2Pqn = 8-(diphenylphosphino)quinoline} and Ag(CF_3SO_3) in methanol afforded orange crystals of the corresponding hydrido complex, [Cp*IrH(Ph_2Pqn)]PF_6, which was identified by ^1H, $^{31}P\{^1H\}$ NMR and IR spectroscopy as well as X-ray structural analysis. The reactions in deuterated solvents indicated that formation of the hydrido complex proceeded via β-H elimination of the coordinated methanol molecule. It was also revealed that the hydrido formation was specific for the complex bearing Ph_2Pqn ancillary ligand; the analogous complex with 1,2-bis(diphenylphosphino)benzene (diphos) or 1,10-phenanthroline (phen) did not give the corresponding hydrido complex by a similar reaction with Ag^+ in methanol. In order to elucidate the reason for the different reactivity among these complexes, the crystal structures of the precursor chlorido complexes, [Cp*IrCl(Ph_2Pqn)]PF_6, [Cp*IrCl(diphos)]PF_6 and [Cp*IrCl(phen)]PF_6, as well as an acetonitrile complex of [Cp*Ir(Ph_2Pqn)(CH_3CN)]$(PF_6)_2$, were also determined by X-ray analysis. The resulting structural information suggested that a specific formation of the hydrido complex with Ph_2Pqn could be originated from the facile formation of the corresponding methanol complex and the hemilabile nature of ancillary Ph_2Pqn ligand, which induced the reactivity of the coordinated methanol toward β-H elimination.

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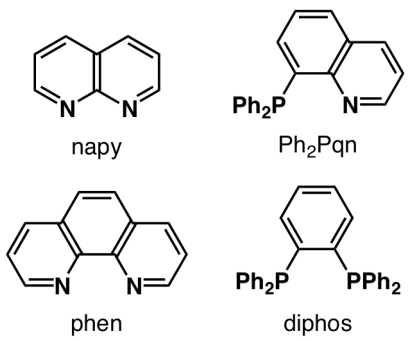
1. Introduction

Pentamethylcyclopentadienyl-iridium(III) or -rhodium(III), Cp^*M^{III} (M = Ir or Rh), are versatile and useful metal fragments for many aspects in coordination and organometallic chemistry, i.e., activation of unreactive bonds or small molecules [1–4], catalytic or stoichiometric chemical transformations [5–14], construction of molecular box or cage compounds [15–17], and so on [18–20]. Octahedral Ir^{III} and Rh^{III} complexes are in general very inert for ligand-substitution, but their Cp* complexes become somewhat hemilabile due to the strong *trans* effect of the Cp* ligand. Also, because the Cp^*M^{III} fragment induces the products to be kinetically and/or thermodynamically stable, the reactive intermediates can often be isolated or detected spectroscopically. Furthermore, these properties lead to prepare a series of Cp^*M^{III} complexes with analogous ligands easily and systematically, and allow to compare their structures and properties in terms of the ancillary ligand effects [20–22]. We have been investigated a number of Cp^*Ir^{III} complexes in this context. For example, photolysis product of the azido complexes of $[Cp^*Ir^{III}(N_3)(L–L)]$ were largely dependent on the ancillary ligand, L–L [23–25]. In the dinuclear complexes of $[\{Cp^*M(L–L)\}_2(\mu\text{-}MeCN_4)]^{n+}$ ($MeCN_4^-$ = 5-methyltetrazolate) it was found that the bridging mode of $MeCN_4^-$ was dependent on the L–L ligands [25,26]. When we tried to prepare several derivatives of Cp*Ir complexes having 1,8-naphthyridine (napy: Scheme 1), we have obtained an interesting hydrido-bridged dinuclear product from a reaction mixture of $[Cp^*IrCl_2(napy)]$ and an equimolar of $AgPF_6$ in a mixture of methanol and dichloromethane. The yield of the complex, $[(Cp^*IrCl)_2(\mu\text{-napy})(\mu\text{-H})]PF_6$ was small, but an isolable amount of the red



Scheme 1 Abbreviations of the ligands used in this study.

crystals were deposited, together with a main product of orange $[Cp^*IrCl(napy)]PF_6$ and another minor by-product of pale yellow $[Cp^*Ir(napy)_2](PF_6)_2$ [27]. Such a formation of Cp^*Ir^{III} hydrido complexes in alcohols was rarely observed [1a,28] and limited to some specific ancillary ligand systems. In this study we will report another example of formation of a Cp^*Ir^{III} hydrido complex when the abstraction of coordinated Cl^- is taken place by Ag^+ ion from $[Cp^*IrCl(Ph_2Pqn)]PF_6$ {**1**; Ph_2Pqn = 8-(diphenylphosphino)quinoline} in methanol. The molecular structure and spectroscopic properties of the product as well as a plausible formation mechanism are described.

2. Experimental section

2.1 Materials and measurements

The ligand, Ph_2Pqn [29], and an iridium(III) complex of $[Cp^*IrCl_2]_2$ [30] were prepared by the literature methods, and other chemicals including 1,10-phenanthroline monohydrate (phen•H_2O), 1,2-bis(diphenylphosphino)benzene (diphos) and deuterated methanol (CD_3OD and CH_3OD) were commercially available, and used as received. Infrared spectra were measured on a JASCO FTIR-001 spectrophotometer using Nujol mull method. Proton and $^{31}P\{^1H\}$ NMR spectra were acquired on a Varian Mercury300 or 400-MR spectrometer at 22 °C. The ^1H NMR chemical shifts were referenced to the residual ^1H NMR signals of the deuterated solvents and are reported versus TMS. The ^{31}P NMR chemical shifts were referenced to the external 85% H_3PO_4.

2.2. Preparation of complexes

*2.2.1. [Cp*IrCl(Ph$_2$Pqn)]PF$_6$ (**1**)*

A methanol solution (10 cm^3) of Ph_2Pqn (161 mg, 0.51 mmol) was added with stirring to a suspension of $[Cp^*IrCl_2]_2$ (205 mg, 0.250 mmol) in methanol (10 cm^3), affording a yellow solution within a few minutes. A methanol solution (5 cm^3) of NH_4PF_6 (160 mg, 0.51 mmol) was added to the resulting solution, depositing a yellow precipitate immediately. The precipitate was collected by filtration, and recrystallized from an acetonitrile solution by vapor diffusion of diethyl ether in a closed vessel. Yield: 357 mg (85%). Anal. Found: C, 45.39; H, 3.56; N, 2.23%. Calcd for $C_{31.5}H_{31.75}ClF_6IrN_{1.25}P_2$ = **1**•0.25CH_3CN: C, 45.50; H, 3.85; N, 2.11%. ^1H NMR (CD_2Cl_2, 22 °C): δ 1.59 (s, Cp*, 15H), 7.04–7.14 (m, 2H), 7.43–7.50 (m, 2H), 7.53–7.68 (m, 4H), 7.77–7.86 (m, 3H), 7.93 (ddd, *J* = 8.1, 7.3 and 1.6 Hz, 1H), 8.18–8.28 (m, 2H), 8.64 (dt, *J* = 8.4 and 1.5 Hz, 1H) and

9.02 (ddd, J = 5.4, 1.4 and 0.5 Hz, 1H). $^{31}P\{^{1}H\}$ NMR (CD_3CN, 22 °C): δ 25.17.

*2.2.2. [Cp*Ir(CH$_3$CN)(Ph$_2$Pqn)](PF$_6$)$_2$ (**2**)*

An acetonitrile solution (5 cm^3) of $AgPF_6$ (153 mg, 0.604 mmol) was added to an acetonitrile solution (2 cm^3) of **1** (495 mg, 0.603 mmol). The mixture was stirred in the dark at ambient temperature for 5 d, and the resulting white precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure, and the residue was extracted with acetone. The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized by vapor diffusion of diethyl ether into an acetonitrile solution, giving pale yellow microcrystals. Yield: 418 mg (70%). Anal. Found: C, 41.06; H, 3.43; N, 2.76%. Calcd for $C_{33}H_{34}IrF_{12}N_2P_3$: C, 40.84; H, 3.40; N, 2.88%. ^{1}H NMR (CD_3CN, 22 °C): δ 1.63 (d, J = 2.5 Hz, Cp*, 15 H), 1.98 (s, CH_3CN, 3H), 7.32–7.42 (m, 2H), 7.55–7.63 (m, 4H), 7.63–7.75 (m, 4H), 7.92 (dd, J = 8.4 and 5.3 Hz, 1H), 8.08 (ddd, J = 8.1, 7.3 and 1.8 Hz, 1H), 8.32 (ddd, J = 10.4, 7.2 and 1.3 Hz, 1H), 8.48 (dt, J = 8.1 and 1.4 Hz, 1H), 8.90 (dt, J = 8.4 and 1.6 Hz) and 9.18 (dd, J = 5.3 and 1.4 Hz, 1H). $^{31}P\{^{1}H\}$ NMR (CD_3CN, 22 °C): δ 26.05.

*2.2.3. [Cp*IrH(Ph$_2$Pqn)]PF$_6$ (**3**)*

A methanol solution (6 cm^3) of $Ag(CF_3SO_3)$ (18 mg, 0.069 mmol) was added with stirring to a suspension of **1** (51 mg, 0.062 mmol) in methanol (4 cm^3). The mixture was allowed to stand in the dark at ambient temperature for a few minutes, and filtered to remove a white precipitate of AgCl. The filtrate was allowed to stand in the dark at ambient temperature for 3 d, and the deposited orange crystals were collected by filtration, and dried in vacuo. Yield: 27 mg (55%). ^{1}H NMR (CD_3CN, 22 °C): δ –13.28 (d, J = 29.8 Hz, 1H, Ir–H), 1.73 (d, J = 2.2 Hz, Cp*, 15 H), 7.73 (dd, J = 13.5 and 7.8 Hz, 2H), 7.69 (ddt, J = 8.1, 6.2 and 2.7 Hz, 4H), 8.05–8.12 (m, 1H), 8.31–8.41 (m, 4H), 8.49 (d, J = 8.2 Hz, 1H), 8.66–8.76 (m, 2H), 8.91 (d, J = 8.4 Hz, 1H) and 9.18 (d, J = 5.6 Hz, 1H). $^{31}P\{^{1}H\}$ NMR (CD_3CN, 22 °C): δ 27.23.

*2.2.4. [Cp*IrCl(diphos)]PF$_6$ (**4**) and [Cp*IrCl(phen)]PF$_6$ (**5**)*

These complexes were prepared by a similar method to that for the Ph_2Pqn complex **1**, using diphos and phen•H_2O, respectively, instead of Ph_2Pqn. The diphos complex, **4**•CH_3CN: yellow block crystals. Yield: 94%. ^{1}H NMR (CD_3CN, 22 °C): δ 1.58 (t, J = 2.3 Hz, Cp*, 15 H), 6.88–6.99

(m, 4H), 7.27–7.37 (m, 5H), 7.48–7.87 (m, 17H). $^{31}P\{^{1}H\}$ NMR (CD_3CN, 22 °C): δ 30.82. The phen complex, **5**: yellow block crystals. Yield: 94%. ^{1}H NMR (CD_3CN, 22 °C): δ 1.74 (s, 15 H), 8.13 (dd, J = 8.2 and 5.3 Hz, 2H), 8.23 (s, 2H), 8.80 (dd, J = 8.2 and 1.3 Hz, 2H), 9.26 (dd, J = 5.3 and 1.3 Hz, 2H).

*2.2.5. Reaction of diphos complex **4** with $AgPF_6$ in acetonitrile*

An acetonitrile solution (3.5 cm^3) of $AgPF_6$ (75.0 mg, 0.296 mmol) was added to an acetonitrile solution (1.5 cm^3) of complex **4** (282 mg, 0.295 mmol), and the mixture was stirred in the dark at room temperature for 2 d. After removal of a small amount of precipitate by filtration, the solution was evaporated to dryness under reduced pressure. The residue was extracted with acetone, and the extract was evaporated, again, to dryness. The crude product was recrystallized from acetonitrile by vapor diffusion of diethyl ether in a closed vessel, recovering the yellow crystals of **4**, which was confirmed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Recovering yield: 150 mg (46%).

*2.2.6. Reaction of diphos complex **4** with $AgPF_6$ in methanol*

A methanol solution (3 cm^3) of $AgPF_6$ (9.3 mg, 0.037 mmol) was added to a methanol suspension (4 cm^3) of complex **4** (34.6 mg, 0.036 mmol), and the mixture was stirred in the dark at room temperature for 2 d. No appreciable precipitate was formed. The mixture was evaporated to dryness by flow of N_2 gas, and the residue was extracted with CD_3CN. The filtered extract was subjected to ^{1}H and $^{31}P\{^{1}H\}$ NMR measurements, which indicated the recovery of complex **4**.

*2.2.7. Reaction of phen complex **5** with $AgPF_6$ in acetonitrile: $[Cp^*Ir(CH_3CN)(phen)](PF_6)_2$ (**6**)*

An acetonitrile solution (2.5 cm^3) of $AgPF_6$ (84.9 mg, 0.336 mmol) was added to an acetonitrile solution (1.5 cm^3) of complex **5** (232 mg, 0.336 mmol), and the mixture was stirred in the dark at room temperature for 2 d. After removal of the resulting white precipitate, the filtered solution was evaporated to dryness under reduced pressure. The residue was extracted with acetone, and the extract was evaporated, again, to dryness. The crude product was recrystallized from acetonitrile by vapor diffusion of diethyl ether in a closed vessel, affording pale yellow crystalline solids. Yield: 250 mg (82%). ^{1}H NMR (CD_3CN, 22 °C): δ 1.74 (s, Cp*, 15 H), 8.21 (dd, J = 8.2 and 5.0 Hz, phen, 2H), 8.28 (s, phen, 2H), 8.91 (d, J = 8.5 Hz, phen, 2H), 9.28 (d, J =

5.5 Hz, phen, 2H).

*2.2.8. Reaction of phen complex **5** with $AgPF_6$ in methanol*

A methanol solution (3 cm^3) of $AgPF_6$ (11.3 mg, 0.044 mmol) was added to a methanol suspension (4 cm^3) of complex **5** (29.3 mg, 0.042 mmol), and the mixture was stirred in the dark at room temperature for 2 d. A white precipitate was formed during the reaction. The mixture was evaporated to dryness by flow of N_2 gas, and the residue was extracted with CD_3CN. The filtered extract was subjected to ^{1}H NMR measurement. ^{1}H NMR (CD_3CN, 22 °C): δ 1.74 (s, Cp*, 15 H), 8.21 (dd, J = 8.7 and 5.5 Hz, phen, 2H), 8.28 (s, phen, 2H), 8.91 (dd, J = 8.0 and 1.2 Hz, phen, 2H), 9.29 (dd, J = 5.5 and 1.5 Hz, phen, 2H).

2.3. Crystallography

The X-ray diffraction data of **1–5** were obtained at –80(2) or –85(2) °C on a Rigaku R-axis rapid imaging plate detector with a graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). A suitable crystal of each complex was mounted with a cryoloop and flash-cooled by cold nitrogen stream. Data were processed by the Process-Auto program package [31], and absorption corrections were applied by the numerical integration method from crystal shape [32]. The structure was solved by the direct method using SIR2004 [33], and refined on F^2 (with all independent reflections) using SHELXL2013 or SHELXL2014 program [34]. All non-H atoms were refined anisotropically, except for one of the Cp* ring carbons of complex **3**, which was refined isotropically. Because the position of the hydrido-H (H1) of complex **3** could not be located in a difference Fourier map, the atom was placed at a hypothetical position and restricted with Ir1–H1 of 1.90 Å and P1–Ir1–H1 and N1–Ir1–H1 angles of 90° in the structural refinement. Other hydrogen atoms were introduced at the positions calculated theoretically and treated with riding models. All calculations were carried out using CrystalStructure software package [35].

Crystal data are collected in Table 1, and selected bond lengths and angles are in Table 2.

3. Results and discussion

3.1. Formation and structural characterization of $[Cp^*IrH(Ph_2Pqn)]PF_6$.

In general, chlorido- (or halido-) abstraction by silver ion from Cp^*Ir^{III} or Cp^*Rh^{III} (Cp^*M) complexes with or without ancillary ligands (L or L–L'), i.e., $[Cp^*MX_2]_2$, $[Cp^*MX_2(L)]$ and $[Cp^*MX(L–L')]^{n+}$, in acetonitrile (or water) gives the corresponding acetonitrile (or aqua) complexes [36], which are conventionally used as precursors for various derivatives of Cp^*Ir^{III} or Cp^*Rh^{III} complexes. In the case of $[Cp^*IrCl(Ph_2Pqn)]PF_6$ (**1**), a reaction with an equivalent amount of $AgPF_6$ in acetonitrile gave yellow crystals of $[Cp^*Ir(Ph_2Pqn)(CH_3CN)](PF_6)_2$ (**2**) in a nearly quantitative yield. However, a similar reaction of **1** with $AgPF_6$ or $Ag(CF_3SO_3)$ in methanol afforded, after removal of the resulting white precipitate (AgCl) and standing the filtrate for a few days, orange crystals of $[Cp^*IrH(Ph_2Pqn)]PF_6$ (**3**) in more than 50% yield. The ^1H NMR spectrum of **3** in CD_3CN showed a doublet resonance for the methyl protons of Cp* at δ 1.73 with the coupling constant of J = 2.2 Hz. The hydride resonance was observed at δ –13.28 as a doublet signal with J = 29.8 Hz. The existence of coordinated hydrido ligand in complex **3** was also confirmed by IR spectroscopy, which gave an absorption at 2129 cm^{-1} attributable to the ν(Ir–H) stretching [37] (Fig. 1*a*).

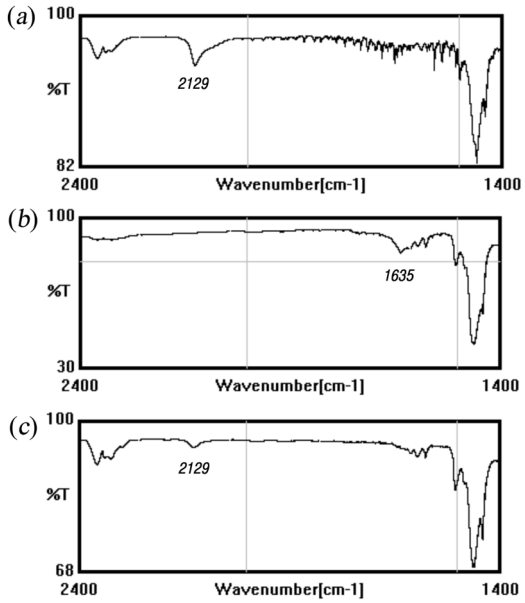


Fig. 1 Infrared spectra of $[Cp^*Ir(H \text{ or } D)(Ph_2Pqn)]PF_6$ (**3** or **3D**) prepared (*a*) in CH_3OH, (*b*) in CD_3OD, and (*c*) in CH_3OD.

The crystal structure of hydrido complex **3**, together with those of complexes **1**•CH_3CN and **2**•CH_3CN, were determined by the X-ray diffraction analysis. The molecular structures of the acetonitrile complex in **2** and the hydrido complex in **3** are shown in Fig. 2. It is obvious that

Ph_2Pqn ligand forms a planar five-membered chelate ring with the bite angle (P1–Ir1–N1) of 81.2(1)–83.0(2)°. The Ir1–N1 bond length in **3** is 2.101(8) Å, which is comparable to those of the other $[Cp^*Ir^{III}(Ph_2Pqn)X]^{n+}$ complexes, i.e., 2.105(3) and 2.104(3) Å of the crystallographically independent two complex cations in **1**•CH_3CN, 2.118(3) Å in **2**•CH_3CN, and 2.115(3) Å in $[Cp^*Ir(N_3)(Ph_2Pqn)]PF_6$•$CH_3OH$ (**7**•CH_3OH) [22a]. In contrast, the Ir–P bond length in **3** is 2.243(2) Å and apparently shorter than those in the other Ph_2Pqn complexes: 2.275(1) and 2.280(1) Å in **1**•CH_3CN, 2.304(1) Å in **2**•CH_3CN, and 2.294(1) Å in **7**•CH_3OH. This is probably due to the steric compactness of a hydrido ligand. The Ir–C bond lengths in **1**•CH_3CN, **2**•CH_3CN, and **7**•CH_3OH are classified into two groups; one is in the range of 2.16–2.20 Å and the other is a little longer as 2.22–2.25 Å, affected by a strong *trans* influence of the diphenylphosphino (Ph_2P) donor group. In complex **3**, two Ir–C bonds are further longer, i.e., Ir1–C2 and Ir1–C3 are 2.274(9) and 2.270(9) Å, respectively. Because these bonds are *transoid* to H1 (see: Fig. 2), the extra elongation of Ir–C bonds in **3** indicates that the *trans* influence of H^- (hydrido) ligand is much stronger than that of Ph_2P donor group.

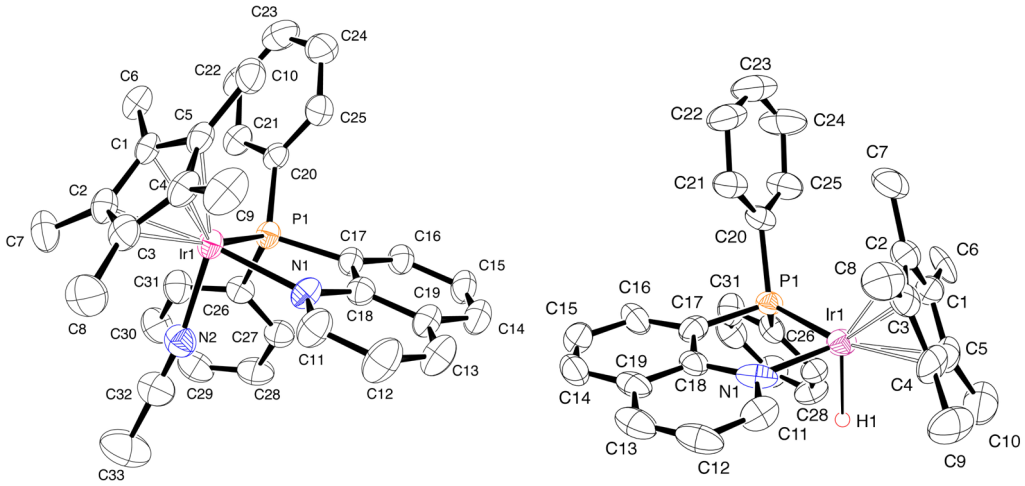


Fig. 2 ORTEPs of the cationic parts in (left) $[Cp^*Ir(Ph_2Pqn)(CH_3CN)](PF_6)_2$•$CH_3CN$ (**2**•CH_3CN) and (right) $[Cp^*IrH(Ph_2Pqn)]PF_6$ (**3**) (50% probability level, H-atoms are omitted for clarity except for the one bound directly to the Ir atom in **3**)

3.2. Experimental approach for the formation mechanism of $[Cp^*IrH(Ph_2Pqn)]^+$

Recently, preparation, characterization and crystal structures of the analogous rhodium(III) chlorido, acetonitrile and hydrido complexes were reported [20]. The molecular and crystal

structures of the chlorido and hydrido complexes are very similar to the above-mentioned iridium(III) analogues. However, the rhodium(III) hydrido complex, [Cp*RhH(Ph_2Pqn)](CF_3SO_3), was synthesized via reduction of the corresponding chlorido complex to [Cp*Rh^{I}(Ph_2Pqn)], followed by addition of anilinium triflate in acentonitrile.

The above-mentioned reaction to afford complex **3** was peculiar, because the iridium(III) hydrido complex was obtained by only abstraction of the coordinated chlorido ligand from the corresponding Cl complex with Ag^+ in methanol, without addition of any common hydride source (or reducing agents, e.g., $CoCp_2$ in the case of Rh^{III} [20]), in a relatively high yield (> 50%). In contrast, a reaction of **1** with Ag^+ in acetonitrile afforded the acetonitrile complex of [Cp*Ir(CH_3CN)(Ph_2Pqn)]$^{2+}$, which were crystallized as the PF_6^- salts (**2**). A similar reaction in a mixture of acetonitrile and water did not give any hydrido complex, either. When the acetonitrile complex **2** was suspended in methanol with stirring for 2 d, formation of the hydrido complex **1** was detected by ^{1}H NMR spectroscopy. Therefore, it was assumed that methanol acted as a hydride source in this reaction. We have attempted to isolate the methanol complex, [Cp*Ir(Ph_2Pqn)(CH_3OH)]$^{2+}$, with various counter anions, but the isolation of this complex as crystalline solids was unsuccessful so far.

In previous studies concerning to the Cp*Ir^{III} hydrido complexes, the mechanism for hydrido formation was discussed and the *β*-hydrogen elimination from the coordinated methanol was proposed [5]. In order to confirm this mechanism, the reaction of complex **1** with Ag(CF_3SO_3) was examined in CD_3OD and in CH_3OD, and the IR spectra of the resulting hydrido/deuterido complexes were compared. The former product showed the ν(Ir–D) stretching band at 1635 cm^{-1} (Fig. 1*b*), which approximately corresponds to the calculated value [37]. In the latter case, a broad absorption due to the ν(Ir–H) was observed at 2129 cm^{-1} (Fig. 1*c*). These results strongly suggest that the hydrido formation of complex **3** was proceeded via *β*-hydrogen elimination mechanism.

The reaction intermediate might be a methoxido complex, because it was proposed that a methoxido complex is a reactive intermediate for alcohol oxidation catalyzed by Cp*Ir(CO_3) complex [7]. To examine this possibility, an acetonitrile solution of sodium methoxide (CH_3ONa, 1 equiv.) was added to an acetonitrile solution of complex **2**; the yellow solution immediately turned to orange. This product seemed to be [Cp*Ir(OCH_3)(Ph_2Pqn)]$^+$, but any hydrido resonance was not detected in the ^{1}H NMR spectrum.

3.3. Ancillary ligand effect for peculiar formation of the hydrido complex.

Because Ph_2Pqn is a hybrid ligand of phosphine and quinoline, a similar Cl^- abstraction with Ag^+ in methanol was examined for the Cp^*Ir^{III} complexes having the related diphosphine or diimine ancillary ligand, 1,2-bis(diphenylphosphino)benzene (diphos) or 1,10-phenanthroline (phen). The complexes of $[Cp^*IrCl(diphos)]PF_6$ (**4**) and $[Cp^*IrCl(phen)]PF_6$ (**5**) were prepared and their reactions with Ag^+ salt were examined. Both in acetonitrile and in methanol, the phen complex **5** reacted with $AgPF_6$, giving a white precipitate of AgCl and the corresponding acetonitrile and methanol complexes of $[Cp^*Ir(phen)(CH_3CN)](PF_6)_2$ and $[Cp^*Ir(phen)(CH_3OH)](PF_6)_2$, respectively, were obtained. The product of $[Cp^*Ir(phen)(CH_3OH)](PF_6)_2$ was gradually turned to green, but any hydrido resonances was not detected in the ^1H NMR spectrum of the decomposed products. In contrast, the diphos complex **4** with $AgPF_6$ (in acetonitrile or in methanol) did not give a precipitate of AgCl after stirring for 2 d, owing presumably to the inertness of the Ir–Cl bond of complex **4**. Therefore, it is claimed that an unusual formation of hydrido complex may be specific to the complexes having an unsymmetrical P–N type ancillary ligand. Here, in order to figure out the reason for the different reactivities toward a Ag^+ ion among the Ph_2Pqn, diphos, and phen complexes, the crystal structures of the chlorido complexes, **1**•CH_3CN, **4**•CH_3CN, and **5**, were determined by X-ray analysis.

Crystal **1** contains two crystallographically independent complex cations in an asymmetric unit, but these two cations are similar in the molecular structures. We expected a different Ir–Cl bond lengths of the diphos complex (**4**•CH_3CN) from the other complexes, since the diphos complex was stable toward the addition of Ag^+. However, the Ir–Cl bond in **4** is 2.395(1) Å which is comparable to those in **1**•CH_3CN (2.408(1) and 2.392(1) Å), in **5** (2.372(1) Å), and $[Cp^*IrCl(phen)]CF_3SO_3$ (2.395(4) Å) [38]. Thus, the Ir–Cl bond lengths can not explain the different reactivity. When we illustrate the surface of complex molecules with van der Waals radii (Fig. 3), it becomes obvious that the Cl^- ligand in the diphos complex is protected effectively by the phenyl and Cp* surroundings, but in the phen complex it is remarkably exposed. In the Ph_2Pqn complex only one side of Cl^- ligand is protected, so that the coordinated Cl^- ligand can be attacked by Ag^+ very easily. This steric protection would be the reason for the observed unreactivity of complex **4** toward the Ag^+ addition.

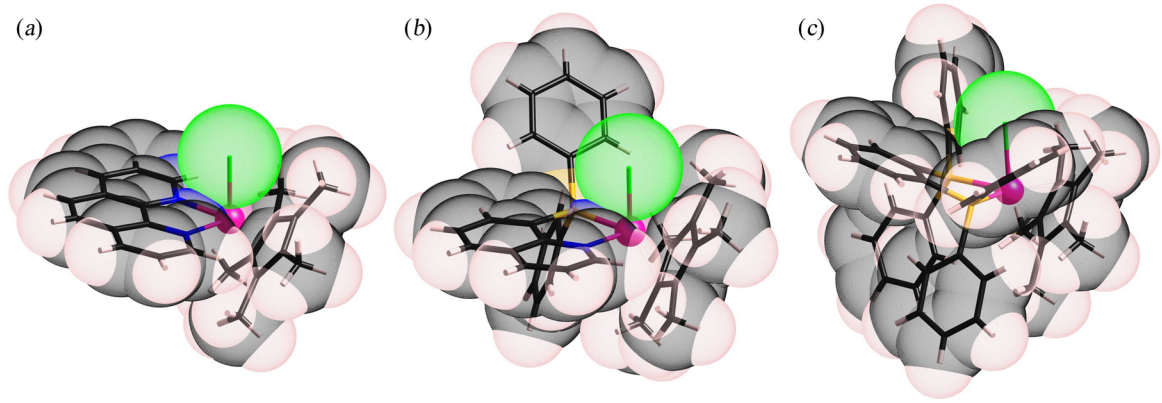
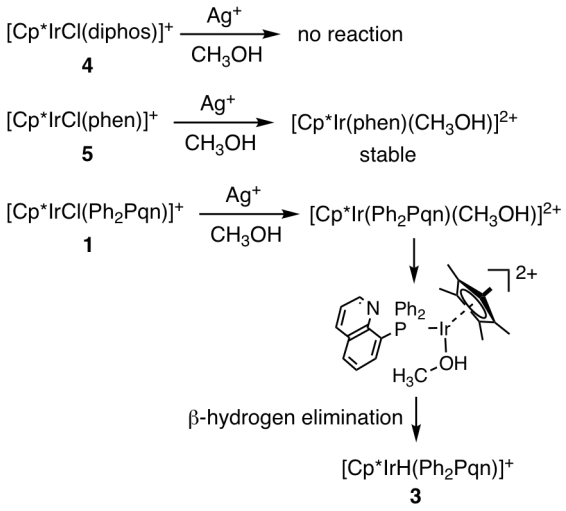


Fig. 3 Van der Waals surfaces of the chlorido complexes of (*a*) $[Cp^*IrCl(phen)]^{2+}$ in **5**, (*b*) $[Cp^*IrCl(Ph_2Pqn)]^{2+}$ in **1**•CH_3CN, and (*c*) $[Cp^*IrCl(diphos)]^{2+}$ in **4**•CH_3CN, resulting from the crystallographic analysis. Color codes: H, pale pink; C, black; N, blue; P, yellow; Ir, purple.

The next question is why the resulting methanol complexes bearing Ph_2Pqn and phen ancillary ligands have a different reactivity toward *β*-hydrogen elimination. It is probable that the methanol complex of $[Cp^*Ir(phen)(CH_3OH)]^{2+}$ is relatively stable, while the coordinating methanol molecule in the Ph_2Pqn complex, $[Cp^*Ir(Ph_2Pqn)(CH_3OH)]^{2+}$, is substantially affected by a steric congestion from the phenyl group of Ph_2Pqn (Fig. 3*b*). Such a steric influence would cause the Ir–N bond in the Ph_2Pqn chelate to be labile, as similarly observed in the bis(Ph_2Pqn) palladium(II) complexes [39]. Then, a transitional 16-e species having a monodentate Ph_2Pqn-κ*P* (Scheme 2) would be formed, which could be an active species for *β*-hydrogen elimination from the coordinated methanol. In this way, the specific formation of hydrido complex having the hybrid-



Scheme 2 Summary of the reactions of complexes **1**, **4** and **5** with Ag^+ in methanol.

type Ph_2Pqn can be explained. Here, we can not exclude a possible bimolecular mechanism (i.e., via agostic interaction of the coordinating methanol molecule in $[Cp^*Ir(Ph_2Pqn)(CH_3OH)]^{2+}$ toward the Cl^--dissociated 16-e species of $[Cp^*Ir(Ph_2Pqn\text{-}\kappa P,N)]^{2+}$). However, the yield of complex **3** in more than 50%, as well as the specificity of this reaction for the hybrid-type Ph_2Pqn ligand, suggest that a proposed mononuclear mechanism with the β-hydrogen elimination would be preferable.

4. Conclusion

A reaction of $[Cp^*IrCl(Ph_2Pqn)]PF_6$ (**1**) and $Ag(CF_3SO_3)$ in methanol afforded orange crystals of the corresponding hydrido complex, $[Cp^*IrH(Ph_2Pqn)]PF_6$ (**3**) in more than 50% yield. Similar reactions in deuterated solvents and that of the acetonitrile complex (**2**) with methanol suggested that the formation of the hydrido complex proceeded via a β-hydrogen elimination from the coordinated methanol ligand. Instead of the Ph_2Pqn complex **1**, the related complexes with an ancillary ligand of diphos or phen were examined for the reaction with Ag^+ salt. In the case of diphos complex **4**, the Cl^- abstraction could not be occurred, probably due to a steric hinderance by the diphos and Cp* ligands. On the contrary, the phen complex **5** afforded a stable methanol complex, but no hydrido formation was detected in the reaction mixture, owing to the efficient stability of the methanol complex. In other words, an unsymmetrical ligand Ph_2Pqn gives a certain open space at the Cl^- ligand for attacking by Ag^+ ion to give the corresponding methanol complex, and the hemilabile nature of hybrid phosphine and quinoline donor groups may give a specific reactivity for the β-elimination to form the hydrido complex. The resulting complex **3** exhibits an interesting reactivity toward, for example, acetone and some acids, which are currently investigating in our laboratory.

Declaration of Competing Interest

The authors declare no conflict of interest in relation to this work.

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Appendix A. Supplementary data

CCDC nos. 1972753–1972757 contains the supplementary crystallographic data for **1**·CH_3CN, **2**·CH_3CN, **3**, **4**·CH_3CN and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from The Cambridge Crystallographic Data Centre, 12 Union Read, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1 Crystallographic data

Compound	**1**•CH_3CN Cl(Ph_2Pqn)	**2**•CH_3CN (Ph_2Pqn)(CH_3CN)	**3** H(Ph_2Pqn)	**4**•CH_3CN Cl(diphos)	**5** Cl(phen)
Chemical formula	$C_{33}H_{34}ClF_6IrN_2P_2$	$C_{35}H_{37}F_{12}IrN_3P_3$	$C_{31}H_{32}F_6IrNP_2$	$C_{42}H_{42}ClF_6IrNP_3$	$C_{22}H_{23}ClF_6IrN_2$
FW	862.21	1012.79	786.71	995.32	688.04
T / K	193(2)	193(2)	188(2)	193(2)	193(2)
Crystal color and shape	yellow, block	yellow, cubic	orange, block	yellow, cubic	yellow, block
Size of specimen / mm	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.2	0.25 × 0.18 × 0.17	0.3 × 0.3 × 0.3	0.3 × 0.2 × 0.2
Crystal system	triclinic	orthorhombic	triclinic	orthorhombic	monoclinic
Space group, *Z*	$P\bar{1}$, 4	*Pbcn*, 8	$P\bar{1}$, 2	*Pbca*, 8	$P2_1/c$, 4
a / Å	8.4694(5)	14.1253(5)	10.1658(9)	19.5792(5)	12.6274(6)
b / Å	15.9703(8)	21.3930(7)	10.4793(11)	17.1486(5)	11.3479(3)
c / Å	25.9778(9)	26.5536(8)	15.2111(18)	23.6205(8)	16.1668(5)
α / °	79.990(2)	90	68.602(3)	90	90
β / °	85.623(2)	90	76.756(3)	90	98.272(1)
γ / °	72.536(2)	90	86.483(3)	90	90
U / $Å^3$	3299.7(3)	8024.0(5)	1468.2(3)	7930.7(4)	2292.52(14)
D_{calc} / Mg m^{-3}	1.736	1.677	1.780	1.667	1.993
μ(Mo Kα) / mm^{-1}	4.285	3.533	4.717	3.616	6.073
R_{int}	0.047	0.037	0.076	0.042	0.046
*R*1 (F^2: $F_o^2 > 2\sigma(F_o^2)$)	0.029	0.030	0.059	0.032	0.017
*wR*2 (F^2: all data)	0.088	0.085	0.1498	0.081	0.041
GoF	1.087	1.060	1.139	1.048	1.064

Table 2 Selected structural parameters (l / Å, ϕ / °)

Compound (X = Cl1, N2, or H1)	**1**•CH_3CN[a] Cl(Ph_2Pqn)	**2**•CH_3CN (Ph_2Pqn)(CH_3CN)	**3** H(Ph_2Pqn)	**7**•CH_3OH[b] (N_3)(Ph_2Pqn)	**4**•CH_3CN Cl(diphos)	**5** Cl(phen)
Ir1–C1	2.222(4), 2.239(4)	2.203(3)	2.191(9)	2.178(3)	2.235(4)	2.153(2)
Ir1–C2	2.247(4), 2.161(4)	2.169(4)	2.274(9)	2.183(3)	2.215(4)	2.190(2)
Ir1–C3	2.179(4), 2.181(4)	2.223(4)	2.270(9)	2.168(4)	2.251(4)	2.161(3)
Ir1–C4	2.183(4), 2.194(3)	2.249(4)	2.227(8)	2.237(4)	2.263(4)	2.148(2)
Ir1–C5	2.172(3), 2.253(4)	2.189(3)	2.194(9)	2.244(4)	2.207(4)	2.146(2)
Ir1–P1	2.2747(9), 2.2802(10)	2.3044(9)	2.243(2)	2.294(1)	2.2866(9)	—
Ir1–P2					2.3023(9)	
Ir1–N1	2.105(3), 2.104(3)	2.118(3)	2.101(8)	2.115(3)	—	2.0983(19)
Ir1–N2						2.112(2)
Ir1–X	2.4081(9), 2.3925(9)	2.055(3)	1.90(2)	2.122(3)	2.3951(9)	2.3719(6)
P1–Ir1–N1	81.85(9), 82.01(9)	81.19(8)	83.0(2)	81.25(9)	—	—
P1–Ir1–P2					84.46(3)	
N1–Ir1–N2						77.32(7)
P1–Ir1–X	90.48(3), 90.05(3)	89.04(9)	90.1(9)	88.48(10)	83.92(3)	—
P2–Ir1–Cl1					85.72(3)	
N1–Ir1–X	79.95(9), 81.92(8)	85.99(12)	89.8(10)	79.10(13)	—	86.02(5)
N2–Ir1–Cl1						83.77(5)

[a] The second values are the corresponding lengths or angles in the other crystallographically independent complex having Ir2. [b] Ref. 22a.